Gibbs Free Energy and Relationships

1) Exams will most likely be graded by Wednesday

2) Regrade requests must be made by section Friday.

3) Free Energy, the puzzle and Temperature, Pressure, Volume and Phase

Reading: Last half of Chapter 3, pp. 84-114, and Chapter 4, pp.123-134

Gibbs Free Energy

The Gibbs Free Energy is a direct measure of spontaneity:

$$G = H - TS$$

It sums up, in a way, the competition between energy considerations and "configurational" barriers.

We have also learned that a process is spontaneous if

$$\Delta G < 0$$

Thus, if

$\Delta H < 0$ the process is exothermic (downhill)
$\Delta S > 0$ the process is increases disorder

So

H dominates spontaneity at low temperatures
S dominates spontaneity at high temperatures

Some instructive examples

$$\mathbf{H_2\,(g) \quad + \quad Cl_2\,(g) \quad \rightarrow \quad 2\,HCl\,(g)}$$

Is ΔS^o_{298} greater than, less than, or equal to zero?

ΔS^o_{298}= -(130.684 + 223.066) + 2 (186.68) J/(K mol)
= **19.61 J / (K mol)**

$$\mathbf{H_2\,(g) \quad + \quad Br_2\,(g) \quad \rightarrow \quad 2\,HBr\,(g)}$$

Is ΔS^o_{298} greater than, less than, or equal to zero?

ΔS^o_{298}= -(130.684 + 245.34) + 2 (198.48) J/(K mol)
= **20.94 J / (K mol)**

Why are these the same? How come they're not zero?

Some instructive examples

C (s,graphite) + O_2 (g) → CO_2 (g)

Is ΔS^o_{298} greater than, less than, or equal to zero?

ΔS^o_{298} = -(5.69 + 205.03) + 213.64 J/(K mol)
= **2.92 J / (K mol)**

Some instructive examples

glycyl-glycine(aq) + $H_2O(l)$ → 2 glycine (aq)

ΔG^o_{298} = -(-490.57 - 237.19) + 2 (-377.69) kJ/mol
= -27.62 kJ/mol

The process is *spontaneous!*

Many proteins have this dipeptide.

How come we don’t spontaneously fall apart?

1) Replenishment
2) Kinetics

But we also have catalysts for this process!

Some instructive examples

$$H_2O(g) \rightarrow H_2(g) + 1/2\ O_2(g)$$

Is ΔS^o_{298} greater than, less than, or equal to zero?

$$\Delta S^o_{298} = -(188.82) + 130.684 + 1/2\ (205.14)\ J/(K\ mol)$$
$$= 44.4\ J\ /\ (K\ mol)$$

Spontaneous?

$$\Delta H^o_{298} = -(-241.82) + 0 + 1/2\ (0)\ kJ/mol = 241.82$$

$$\Delta G^o_{298} = \Delta H^o_{298} - T\ \Delta S^o_{298} = 241.82\ kJ/mol - (298\ K)*0.0444\ kJ/(K\ mol)$$
$$= 228.56\ kJ/mol$$

The process is *non-spontaneous!*

Gibbs Free Energy: Basic Dependencies

So we have defined ΔG as:

$$\Delta G = \Delta H - \Delta(TS)$$

We can substitute for ΔH :

$$\Delta G = \Delta E + \Delta pV - \Delta TS$$

$$dG = dE + pdV + Vdp - TdS - SdT$$

Then for systems doing PV work *only*

$$dG = dq - pdV + pdV - VdP -TdS - SdT$$
$$= dq + VdP - TdS - S\,dT$$

Remembering that TdS ≥ dq

$$dG \le TdS + VdP -TdS - SdT$$
$$dG \le +VdP-SdT$$

So for an open system at constant T and P, the criterion for spontaneity is:

$$dG \le 0 \begin{cases} \text{Spontaneous} \\ \text{Equilibrium} \end{cases}$$

We only need the sign of ΔG

Gibbs Free Energy

A puzzle:

at constant T and p,

$$\Delta G = \Delta E + p\Delta V - T\Delta S$$

Assume everything is reversible.

$$\Delta E = w + q$$
$$\Delta S = q/T$$

so $\Delta G = w + p\Delta V$

but $w = -p\Delta V$

Hence, $\Delta G = 0$???

According to this, we can't ever have ΔG < 0 if everything is reversible at constant T and p. But what about all those chemical reactions? Surely they can be run reversibly! But $\Delta G \neq 0$

Where is the mistake?

What's the error?

A puzzle:

at constant T and p,

$$\Delta G = \Delta E + p\Delta V - T\Delta S$$

Assume everything is reversible.

$$\Delta E = w + q$$

$$\Delta S = q/T$$

so $\Delta G = w + p\Delta V$

but $\boxed{w = -p\Delta V}$

Hence, $\Delta G = 0$???

Not all work is PV work! For example, electrochemical, mechanical, etc.

"Free" means free to do non-PV work!

Temperature Dependence

First remember that:

$$\Delta S = \int \frac{dq_{rev}}{T} = \int_{T_1}^{T_2} \frac{C_P dT}{T}$$

$$\left(\frac{dq}{dT}\right)_P = C_P$$

If we hold P constant for a reversible process then:

$$\Delta G = V\Delta P - S\Delta T = -\int_{T_1}^{T_2} S(T)dT = -\int_{T_1}^{T_2} (S(T_1) + \frac{C_P}{T})dT$$

This can be made even more exact if $C_P(T)$ has been measured.

Temperature Dependence

If we assume that ΔS and ΔH are constant over a small temperature range we can calculate ΔG at different temperatures easily:

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G(T) - \Delta G(298K) \approx -(T - 298K)\Delta S(298K)$$

$$or$$

$$\frac{\Delta G(T)}{T} - \frac{\Delta G(298K)}{298K} \approx \left(\frac{1}{T} - \frac{1}{298K}\right)\Delta H(298K)$$

Obviously, if ΔS and ΔH depend greatly on T then we must proceed as before!

Temperature Dependence: Example

For glycl-glycine hydrolysis then:

ΔS^o_{298}= 2(103.51) - 190 - 69.5 J/(K mol)
= -52.9 J / (K mol)

ΔH^o_{298}= 2(-537.2) - (-745.25)- (-285.83) kJ/(mol)
= -43.32 kJ / (mol)

Plugging and chugging!

$$\Delta G(37^\circ C) \approx (310-298)\Delta S(298K) + \Delta G(298K) = -26.99 kJ / mol$$

$$\frac{\Delta G(37^\circ C)}{310K} \approx \left(\frac{1}{310} - \frac{1}{298K}\right)\Delta H(298K) + \frac{\Delta G(298K)}{298K} = -26.99 kJ / mol$$

Pressure Dependence: Example

For the pressure dependence we hold T constant:

$$dG \leq VdP\text{-}SdT\text{=-}VdP$$

Thus,

$$\Delta G = \int_{1}^{2} VdP$$

And for an ideal gas:

$$\Delta G = \int_{1}^{2} VdP = \int_{P_1}^{P_2} \frac{nRT}{P} dP = nRT \ln(\frac{P_2}{P_1})$$

Does the free energy behave as expected?
Note that unlike in the puzzle, P is not constant!

Can we force graphite to diamond by increasing the pressure? We will use:

$$\Delta G = \int_1^2 V dP$$

and the fact that molar volumes of graphite and diamond are known:

$$\bar{V} = weight / density$$

$$\bar{V}_{graphite} = 5.33 cm^3 / mol$$

$$\bar{V} diamond = 3.42 cm^3 / mol$$

$$\Delta G(P) = \Delta G(1atm) + \Delta V * (P - 1)$$

$$\Delta G(P) = 2.84 - 1.935 * 10^{-4} * (P - 1)$$

Where we have used a conversion factor to convert from cm^3 atm to kJ.

Now, we want the pressure that makes $\Delta G=0$: ***Why?***

$$0 = 2.84 - 1.935\ 10^{-4}\ (P-1)\ \text{kJ/mol}$$

$$P = 15{,}000\ \text{atm}$$

Experimentally, the required pressure is more! ***Why?***

Homework

Reading: Last half of Chapter 3, pp. 84-114, and Chapter 4, pp.123-134

TSW: 3.13, 3.22(d,f), 3.23,3.26

In a hypothetical cell, the steady-state concentrations of a phosphorylated intermediate, R-O-p, and its hydrolysis product, R-OH + P_i are 0.02 M, 0.0004 M, and 0.05 M, respectively. The ΔG° of the hydrolysis reaction is -8.22 kcal/mol.

$$\text{R-O-P} + H_2O \longrightarrow \text{R-OH} + P_i$$

a) Calculate the equilibrium constant for the hydrolysis reaction.
b) Is the steady-state cited anywhere near equilibrium?
c) Would you classify R-O-P as a high energy phosphate compound? Give ΔG° for the following reaction.

$$\text{R-O-P} + \text{ADP} \longrightarrow \text{R-O-H} + \text{ATP}$$